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According to yet another aspect of the invention the tetramerisation process includes the step of contacting an olefinic feedstream with a catalyst system which includes a transition metal and a heteroatomic ligand and wherein the product of the tetramerisation process is an olefin and the olefin is concomitantly copolymerised with the olefinic feedstream by contacting the olefins produced in the first step and the olefinic feedstream with a catalyst comprising of a transition metal and/or a homo- or heteroatomic ligand.

By homoatomic is meant a ligand that consists entirely of similar atoms such as carbon that constitute the skeleton of the ligand such as the cyclopentadienyl ligand for example.

The ethylene to be tetramerised and polymerised can be introduced into the process according to the invention in a continuous or batch fashion.

The tandem catalysis product stream will be understood to include a polymer, which polymer is produced according to the invention in a continuous or batch fashion.

The process may include a process for tetramerisation of ethylene to selectively yield 1-octene.

The process may be a process for tetramerisation of ethylene and concomitant polymerisation of the produced 1-octene with ethylene .

The ethylene may be contacted with the catalyst system comprising of the tetramerisation catalyst and the polymerisation catalyst at a pressure of 1 barg, preferably greater than 10 barg, more preferably greater than 30 barg.

The tandem catalysis process may include the step of mixing the components of the catalyst systems (both the tetramerisation catalyst and the polymerisation catalyst) at any temperature between -20°C and 250°C in the presence of an olefin. The preferred temperature range being 20 °C - 100 °C.

The individual components of both catalyst systems described herein may be combined simultaneously or sequentially in any order, and in the presence or absence of a solvent, in order to give active catalysts. The presence of an olefin during the mixing of the catalyst components generally provides a protective effect which may result in improved catalyst performance. The preferred temperature range may be between 20°C and 100°C.

The reaction products derived from the tandem catalysis process as described herein, may be prepared using the disclosed catalyst system by a homogeneous liquid phase reaction in the presence or absence of an inert solvent, and/or by slurry reaction where the catalyst system is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which neat reagent and/or product olefins serve as the dominant medium, and/or gas phase reaction, using conventional equipment and contacting techniques.

The tandem catalysis process may also be carried out in an inert solvent. Any inert solvent that does not react with the activator can be used. These inert solvents may include, saturated aliphatic, unsaturated aliphatic, aromatic hydrocarbon and halogenated hydrocarbon. Typical solvents include, but are not limited to, benzene, toluene, xylene, cumene, heptane, methylcyclohexane, methylcyclopentane, cyclohexane, ionic liquids and the like.

The tandem catalysis process may be carried out at pressures from atmospheric to 500 barg. Ethylene pressures in the range of 10-70 barg are preferred. Particularly preferred pressures range from 30-50 barg.

The tandem catalysis process may be carried out at temperatures from -20 °C - 250 °C. Temperatures in the range of 15-130 °C are preferred. Particularly preferred temperatures range from 35-150°C.

The tandem catalysis process may be carried out in a plant which includes any type of reactor. Examples of such reactors include, but are not limited to, batch reactors, semi-batch reactors and continuous reactors. The plant may include, in combination a) a reactor, b) at least one inlet line into this reactor for olefin reactant and the catalyst

A solution of 9.8 mg of (*p*-methoxyphenyl)₂PN(isopropyl)P(*p*-methoxyphenyl)₂ (0.018 mmol) in 10 ml of toluene was added to a solution of 5.6 mg CrCl₃(THF)₃ (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.0831 g of polyethylene. The GC analyses indicated that the reaction mixture contained 42.72 g oligomers. The oligomers comprised 72% 1-octene (99% purity).

Example 2: Ethylene tetramerisation reaction using Cr(acetylacetonate)₃, (phenyl)₂PN(isopropyl)P(phenyl)₂ and MAO

A solution of 18.8 mg of (phenyl)₂PN(isopropyl)P(phenyl)₂ (0.044 mmol) in 6.4 ml of cumene was added to a solution of 7.7 mg Cr(acetylacetonate)₃ (0.022 mmol) in 8 ml cumene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 1000 ml pressure reactor (autoclave) containing a mixture of cumene (180 ml) and MAO (methylaluminoxane, 4.4 mmol, 10 % solution in toluene) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 45 barg. The reaction was terminated after 25 min, and the procedure of Example 2 above was employed. The product mass was 118.78 g. The product comprised 69.5% 1-octene (98.9% purity).

Example 3: Tandem catalysis reaction using $\text{Cr}(\text{acetylacetonate})_3$, $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$, MAO and dimethylsilyl-bis(2-methyl{4,5}benzoindenyl) zirconium dichloride

In this example, 0.011 mmol Chromium acetylacetonate (15.2 mg) was combined with 0.022 mmol $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$ (36 mg) in a Schlenk tube under an argon atmosphere with 10 ml anhydrous toluene as solvent. The metal salt and the ligand was stirred for 5 minutes and then added under inert conditions to a Parr autoclave (300 ml capacity). The autoclave was filled *a priori* with 70 ml anhydrous toluene as solvent. Separately, 2 ml of a solution of dimethylsilyl-bis(2-methyl(4,5)benzoindenyl) zirconium dichloride (0.0052 mmol, 0.0022 mg) was added to 18 ml anhydrous toluene in a separate reservoir under inert conditions connected to the inlet of an HPLC pump. Approximately 1200 eq (on Cr) methylaluminoxane (MAO) was added to the autoclave under argon atmosphere. The autoclave was heated to 45 °C, sealed and pressurised to 35 barg with ethylene whilst stirring was commenced at 1200 rpm. At the same time the polymerisation catalyst solution was added to the autoclave through an inlet on the Parr reactor that was connected to the outlet of the HPLC pump. The polymerisation catalyst was added at a rate of 0.66 ml/min over a period of 30 minutes after which the reaction vessel was cooled down and quenched with ethanol. After 30 minutes, the autoclave was opened and the contents collected for analysis. The amount of polymer collected was found to be 23.16 g with a melting point of 126 °C and an amount of 1-octene incorporation as determined by ^{13}C nuclear magnetic resonance spectroscopy of 3.83 %.

Example 4: Tandem catalysis reaction using $\text{Cr}(\text{acetylacetonate})_3$, $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$, MAO and tetramethylcyclopentadienyl dimethylsilyl t-butylamidato titanium dichloride

In this example, a solution of 20 ml $(\text{phenyl})_2\text{PN}(\text{iso-propyl})\text{P}(\text{phenyl})_2$ (0.044 mmol) in anhydrous toluene and 20 ml of a solution of $\text{Cr}(\text{acetylacetonate})_3$ (0.022 mmol) in 30 ml

anhydrous toluene was added to a Parr autoclave (300 ml capacity). At the same time, 10 ml of a solution of tetramethylcyclopentadienyl-dimethylsilyl-t-butylamido titanium dichloride (0.026 mmol, 0.01 mg) was added to an external reservoir along with 10 ml anhydrous toluene. The external reservoir (under argon atmosphere) was connected to the inlet of an HPLC pump. Approximately 1200 eq (on Cr) methylaluminoxane (MAO) was added to the autoclave under inert conditions. The autoclave was heated to 45 °C, sealed and pressurised to 43 barg with ethylene whilst stirring was commenced at 1200 rpm. At the same time the polymerisation catalyst solution was added to the autoclave through a separate inlet on the Parr reactor that was connected to the outlet of the HPLC pump. The polymerisation catalyst was added at a rate of 0.66 ml/min over a period of 30 minutes after which the reaction vessel was cooled down and quenched with ethanol. The autoclave was opened and the contents collected for analysis. Analysis of the polymer after drying in vacuum for 12 h at 60 °C revealed a melting point of 99 °C and 2.39 % incorporation of 1-octene as determined using ^{13}C NMR. The amount of polymer collected was 24.53g. The density of the polymer was determined to be 0.9202 g.cm^{-3} .

Example 5: Tandem catalysis reaction using (p-methoxyphenyl) $_2$ PN(isopropyl)P(p-methoxyphenyl) $_2$, Cr(acetylacetonate) $_3$, MAO and dimethylsilyl bisindenyl zirconium dichloride

In this example, 10 ml of a toluene solution containing 0.03 mmol chromium acetylacetonate was combined with 0.06 mmol (p-methoxyphenyl) $_2$ PN(isopropyl)P(p-methoxyphenyl) $_2$ [30 mg] in a Schlenk tube under an argon atmosphere. The metal salt and the ligand was stirred for 5 minutes and then added to a Parr autoclave (300 ml capacity) under inert conditions. The autoclave was filled *a priori* with 60 ml anhydrous toluene as solvent. Separately, 5 ml of a solution of dimethylsilyl bisindenyl zirconium dichloride (0.015 mmol, 0.0067 mg), was added to 15 ml anhydrous toluene in a separate reservoir under argon that was connected to the inlet of an HPLC pump. Approximately 600 eq (on Cr) methylaluminoxane (MAO) was added to the autoclave under inert conditions. The autoclave was heated to 45 °C, sealed and pressurised to a pressure of 41 barg with ethylene whilst stirring was commenced at 1200 rpm. At the same time the polymerisation catalyst solution was added to the autoclave through a separate inlet connected to the outlet of the HPLC pump. The polymerisation catalyst

was added at a rate of 0.33 ml/min over a period of 60 minutes after which the reaction vessel was cooled down and quenched with ethanol. The autoclave was opened and the contents collected for analysis. The amount of polymer collected was first dried in a vacuum oven at 60 °C for 12 h yielding an amount of 51.1 g with a melting point of 106 °C and an amount of 1-octene incorporated as determined by ^{13}C nuclear magnetic resonance spectroscopy of 5.55 %. The density of the polymer was determined to be 0.8155 g.cm^{-3} .

Example 6: Tandem catalysis reaction using (p-methoxyphenyl)₂-PN(isopropyl)P(p-methoxyphenyl)₂, Cr(acetylacetonate)₃, MAO and cyclopentadienyl dimethylsilyl titanium dichloride

In this example, 0.025 g of (p-methoxyphenyl)₂-PN(isopropyl)P(p-methoxyphenyl)₂ [0.06 mmol] was added to 10 ml of a toluene solution of Cr(acetylacetonate)₃ (0.03 mmol) in a Schlenk tube under an argon atmosphere and allowed to stir for 5 minutes until fully dissolved. At the same time, 10 ml of a cyclopentadienyl dimethylsilyl titanium dichloride (0.03 mmol, 0.009 mg) solution in toluene was added to an external reservoir along with 10 ml anhydrous toluene. The external reservoir was connected to the inlet of an HPLC pump. After this, the 300 ml Parr autoclave was charged with 60 ml anhydrous toluene as well as the previously stirred Cr(acetylacetonate)₃/(p-methoxyphenyl)₂-PN(isopropyl)P(p-methoxyphenyl)₂ ligand solution under inert conditions. Approximately 600 eq (on Cr) methylaluminoxane (MAO) was added to the autoclave under inert conditions. The autoclave was connected to the HPLC pump outlet and heated to 45 °C, sealed and pressurised to a pressure of 53 barg with ethylene for the duration of the reaction (60 minutes) whilst stirring was commenced at 1200 rpm. At the same time the polymerisation catalyst solution was added to the autoclave through the HPLC pump. The polymerisation catalyst was added at a rate of 0.33 ml/min over a period of 60 minutes after which the reaction vessel was cooled down and quenched with ethanol. The autoclave was opened and the contents collected for analysis. The polymer collected was washed in acetone and dried in a vacuum oven for 12h at 60 °C. The dried polymer amounted to 3.35 g. Analyses of the polymer revealed a melting point of 128 °C and 1.02 % incorporation of 1-octene as determined by ^{13}C NMR.

Claims

1. A process for polymerising olefins to branched polyolefins in the presence of a polymerisation catalyst and a cocatalyst, wherein the cocatalyst produces 1-octene in a selectivity greater than 30%.
2. A process as claimed in Claim 1 wherein the branched polyolefin is a branched polyethylene.
3. A process as claimed in Claim 1 or Claim 2 wherein the branched polyolefin is linear low density polyethylene.
4. A process as claimed in any one of the preceding claims wherein the cocatalyst is an ethylene tetramerisation catalyst.
5. A process as claimed in Claim 4 wherein the ethylene tetramerisation catalyst includes a transition metal and a heteroatomic ligand.
6. A process as claimed in Claim 5 wherein the heteroatomic ligand is described by a general formula $(R)_nA-B-C(R)_m$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium, and nitrogen, and B is a linking group between A and C, and the R groups are the same or different and each R is independently selected from any homo or heterohydrocarbyl group and n and m for each R is independently determined by the respective valence and oxidation state of A and C.
7. A process as claimed in Claim 5 or Claim 6 wherein the heteroatomic ligand is described by a general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, bismuth and nitrogen and B is a linking group between A and C, and R^1 , R^2 , R^3 and R^4 are independently selected from hydrocarbyl or

heterohydrocarbyl or substituted hydrocarbyl or substituted heterohydrocarbyl groups.

8. A process as claimed in any one of claims 5 to 7, wherein the heteroatomic ligand is described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, bismuth, and nitrogen and B is a linking group between A and C, and R^1 , R^2 , R^3 and R^4 are independently non-aromatic or aromatic, including heteroaromatic, groups.
9. A process as claimed in Claim 8, wherein R^1 , R^2 , R^3 and R^4 are independently aromatic, including heteroaromatic groups and not all the groups R^1 , R^2 , R^3 and R^4 have a substituent on the atom adjacent to the atom bound to A or C.
10. A process as claimed in Claim 9, wherein not more than two of R^1 , R^2 , R^3 and R^4 have substituents on the atom adjacent to the atom bound to A or C.
11. A process as claimed in Claim 9 or Claim 10 wherein at least one or more of R^1 , R^2 , R^3 and R^4 are substituted with a polar substituent on a second or further atom from the atom bound to A or C.
12. A process as claimed in any one of claims 9 to 11, wherein any polar substituents on R^1 , R^2 , R^3 and R^4 are not on the atom adjacent to the atom bound to A or C.
13. A process as claimed in Claim 11 or Claim 12 wherein any polar substituent on one or more of R^1 , R^2 , R^3 and R^4 are electron-donating.
14. A process as claimed in Claim 9 or Claim 10, wherein any substituents on one or more of R^1 , R^2 , R^3 and R^4 are not electron-donating.
15. A process as claimed in Claim 14 wherein each non-electron donating substituent is non-polar.

16. A process as claimed in any one of claims 10 to 15 wherein each of R^1 , R^2 , R^3 and R^4 is aromatic, including heteroaromatic, but not all of R^1 , R^2 , R^3 and R^4 are substituted by any substituent on an atom adjacent to the atom bound to A or C.
17. A process as claimed in any one of claims 6 to 16, wherein B is selected from any one of a group comprising: organic linking groups comprising a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl; inorganic linking groups comprising single atom links; ionic links and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, $-B(R^5)-$, $-Si(R^5)_2-$, $-P(R^5)-$ and $-N(R^5)-$ where R^5 is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom, a halogen, a cyclic heteroatomic group or a cyclic homoatomic group.
18. A process as claimed in Claim 17 wherein B is selected to be a single atom spacer.
19. A process as claimed in Claim 17 or Claim 18, wherein B is selected to be $-N(R^5)-$, wherein R^5 is hydrogen or selected from the groups consisting of alkyl, aryl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, aryl substituted with any of these substituents, and any cyclic heteroatomic group including cyclopentadienyl dimethylsilyl-t-butylamidato or a cyclic homoatomic group including cyclopentadienyl, indenyl and fluorene.
20. A process as claimed in any one of claims 6 to 19, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.
21. A process as claimed in Claim 20, wherein A and/or C is independently phosphorus or phosphorus oxidised by S or Se or N or O.
22. A process as claimed in any one of claims 7 to 21, wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group comprising a benzyl, phenyl, tolyl, xylyl,

mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl, thiophenoxy, trimethylsilyl, dimethylhydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and tetrahydrofuranyl group.

23. A process as claimed in any one of claims 7 to 21 wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group comprising a phenyl, tolyl, biphenyl, naphthyl, thiophenyl and ethyl group.
24. A process as claimed in any one of claims 5 to 9, Claim 14 and Claim 15 wherein the heteroatomic ligand is selected from any one of a group comprising
- | | |
|---|---|
| (phenyl) ₂ PN(methyl)P(phenyl) ₂ , | (phenyl) ₂ PN(pentyl)P(phenyl) ₂ , |
| (phenyl) ₂ PN(phenyl)P(phenyl) ₂ , | (phenyl) ₂ PN(p-methoxyphenyl)P(phenyl) ₂ , |
| (phenyl) ₂ PN(p- ^t -butylphenyl)P(phenyl) ₂ , | (phenyl) ₂ PN((CH ₂) ₃ -N-morpholine)P(phenyl) ₂ , |
| (((phenyl) ₂ P) ₂ NCH ₂ CH ₂)N, | (phenyl) ₂ PN(Si(CH ₃) ₃)P(phenyl) ₂ , |
| (ethyl) ₂ PN(methyl)P(ethyl) ₂ , | (ethyl) ₂ PN(isopropyl)P(phenyl) ₂ , |
| (ethyl)(phenyl)PN(methyl)P(ethyl)(phenyl), | (phenyl) ₂ P(=Se)N(isopropyl)P(phenyl) ₂ , |
| (phenyl) ₂ PCH ₂ CH ₂ P(phenyl) ₂ , | (o-ethylphenyl)(phenyl)PN(isopropyl)P(phenyl) ₂ , |
| (o-methylphenyl) ₂ PN(isopropyl)P(o-methylphenyl)(phenyl), | (phenyl) ₂ PN(benzyl)-P(phenyl) ₂ , |
| (phenyl) ₂ PN(1-cyclohexylethyl)P(phenyl) ₂ , | (phenyl) ₂ PN[CH ₂ CH ₂ CH ₂ Si(OMe) ₃]P(phenyl) ₂ , |
| (phenyl) ₂ PN(cyclohexyl)P(phenyl) ₂ , | (phenyl) ₂ PN(2-methylcyclohexyl)P(phenyl) ₂ , |
| (phenyl) ₂ PN(allyl)P(phenyl) ₂ , | (o-naphthyl) ₂ PN(methyl)P(o-naphthyl) ₂ , |
| (p-biphenyl) ₂ PN(methyl)P(p-biphenyl) ₂ , | (p-Me-phenyl) ₂ PN(methyl)P(p-Me-phenyl) ₂ , |
| (o-thiophenyl) ₂ PN(methyl)P(o-thiophenyl) ₂ , | (phenyl) ₂ PN(methyl)N(methyl)P(phenyl) ₂ , |
| (m-Me-phenyl) ₂ PN(methyl)P(m-Me-phenyl) ₂ , | (phenyl) ₂ PN(isopropyl)P(phenyl) ₂ , |
| (phenyl) ₂ P(=S)N(isopropyl)P(phenyl) ₂ , | |
| (phenyl) ₂ P(=S)N(isopropyl)P(=S)(phenyl) ₂ , | and |
25. A process as claimed in any one of claims 5 to 13, wherein the heteroatomic ligand is selected from any one of a group comprising ((*m*-methoxyphenyl)₂PN(methyl)P(*m*-methoxyphenyl)₂,
- (*p*-

methoxyphenyl)₂PN(methyl)P(*p*-methoxyphenyl)₂, (m-
 methoxyphenyl)₂PN(isopropyl)P(*m*-methoxyphenyl)₂, (*p*-
 methoxyphenyl)₂PN(isopropyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(2-
 ethylhexyl)P(*p*-methoxyphenyl)₂, (m-
 methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂ and (*p*-
 methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂, (m-
 methoxyphenyl)(phenyl)PN(methyl)P(*m*-methoxyphenyl)(phenyl), (*p*-
 methoxyphenyl)(phenyl)PN(methyl)P(*p*-methoxyphenyl)(phenyl), (m-
 methoxyphenyl)₂PN(methyl)P(phenyl)₂ and (*p*-
 methoxyphenyl)₂PN(methyl)P(phenyl)₂, (*p*-methoxyphenyl)₂PN(1-
 cyclohexylethyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(2-
 methylcyclohexyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(decyl)P(*p*-
 methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(pentyl)P(*p*-methoxyphenyl)₂, (*p*-
 methoxyphenyl)₂PN(benzyl)P(*p*-methoxyphenyl)₂, (*p*-
 methoxyphenyl)₂PN(phenyl)P(*p*-methoxyphenyl)₂, (*p*-
 fluorophenyl)₂PN(methyl)P(*p*-fluorophenyl)₂, (*o*-fluorophenyl)₂PN(methyl)P(*o*-
 fluorophenyl)₂, (*p*-dimethylamino-phenyl)₂PN(methyl)P(*p*-dimethylamino-phenyl)₂,
 (*p*-methoxyphenyl)₂PN(allyl)P(*p*-methoxyphenyl)₂, (phenyl)₂PN(isopropyl)P(*o*-
 methoxyphenyl)₂, (*p*-(*p*-methoxyphenyl)-phenyl)₂PN(isopropyl)P(*p*-(*p*-
 methoxyphenyl)-phenyl)₂ and (*p*-
 methoxyphenyl)(phenyl)PN(isopropyl)P(phenyl)₂.

26. A process as claimed in any one of the preceding claims wherein the polymerisation catalyst is selected from a group of catalysts consisting of Ziegler-Natta catalysts, unbridged metallocenes, half sandwich metallocenes, methyl-bridged metallocenes, ethyl-bridged metallocenes and silyl-bridged metallocenes.
27. A process as claimed in Claim 26, wherein the Ziegler-Natta catalyst is selected from TiCl₃-Et₂AlCl, AlR₃-TiCl₄.
28. A process as claimed in Claim 26 wherein the unbridged metallocene is selected from:
 bis(cyclopentadienyl)chromium(II),

bis(cyclopentadienyl)-zirconium Chloride hydride,
bis(cyclopentadienyl)-titanium dichloride,
bis(cyclopentadienyl)-zirconium dichloride,
bis(cyclopentadienyl)-zirconium dimethyl,
bis(*n*-butylcyclopentadienyl)-zirconium dichloride,
bis(*n*-dodecylcyclopentadienyl)-zirconium dichloride,
bis(ethylcyclopentadienyl)-zirconium dichloride,
bis(iso-butylcyclopentadienyl)-zirconium dichloride,
bis(isopropylcyclopentadienyl)-zirconium dichloride,
bis(methylcyclopentadienyl)-zirconium dichloride,
bis(*n*-octylcyclopentadienyl)-zirconium dichloride,
bis(*n*-pentylcyclopentadienyl)-zirconium dichloride,
bis(*n*-propylcyclopentadienyl)-zirconium dichloride,
bis(trimethylsilylcyclopentadienyl)-zirconium dichloride,
bis(1,3-bis(trimethylsilyl)cyclopentadienyl)-zirconium dichloride,
bis(1-ethyl-3-methylcyclopentadienyl)-zirconium dichloride,
bis(pentamethylcyclopentadienyl)-zirconium dichloride,
bis(pentamethylcyclopentadienyl)-zirconium dimethyl,
bis(1-propyl-3-methylcyclopentadienyl)-zirconium dichloride,
bis(4,7-dimethylindenyl)-zirconium dichloride,
bis(indenyl)-zirconium dichloride,
bis(2-methylindenyl)-zirconium dichloride,
bis(2-methylindenyl)-zirconium dichloride, and
cyclopentadienylindenyl-zirconium dichloride.

29. A process as claimed in Claim 26, wherein the half sandwich metallocene is selected from:

Cyclopentadienyl-zirconium trichloride,
pentamethylcyclopentadienyl titanium trichloride,
pentamethylcyclopentadienyl-titanium Trimethoxide,
pentamethylcyclopentadienyl-titanium Trimethyl,
pentamethylcyclopentadienyl-zirconium trichloride,
tetramethylcyclopentadienyl-zirconium trichloride, and
1,2,4-trimethylcyclopentadienyl-zirconium trichloride.

30. A process as claimed in Claim 26, wherein the carbon-bridged metallocene is selected from:
Diphenylmethylidene(cyclopentadienyl)-(9-fluorenyl)-zirconium dichloride,
diphenylmethylidene(cyclopentadienyl)-(indenyl)-zirconium dichloride,
iso-propylidenebis(cyclopentadienyl)-zirconium dichloride,
iso-propylidene(cyclopentadienyl)(9-fluorenyl)-zirconium dichloride, and
iso-propylidene(3-methylcyclopentadienyl)-(9-fluorenyl)-zirconium dichloride.
ethylene-bis(9-fluorenyl)-zirconium dichloride,
meso-ethylene-bis(1-indenyl)-zirconium dichloride,
rac-ethylene-bis(1-indenyl)-zirconium dichloride,
rac-ethylene-bis(1-indenyl)-zirconium dimethyl,
rac-ethylene-bis(2-methyl-1-indenyl)-zirconium dichloride, and
rac-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)-zirconium dichloride
32. A process as claimed in Claim 26, wherein the silyl-bridged metallocene is selected from:
Dimethylsilyl-bis(cyclopentadienyl)-zirconium dichloride,
dimethylsilyl-bis(9-fluorenyl)-zirconium dichloride,
rac-dimethylsilyl-bis(1-indenyl)-zirconium dichloride,
meso-dimethylsilyl-bis(2-methylindenyl)-zirconium dichloride,
rac-dimethylsilyl-bis(2-methylindenyl)-zirconium dichloride,
rac-dimethylsilyl-bis(tetrahydroindenyl)-zirconium dichloride,
dimethylsilyl-bis(tetramethylcyclopentadienyl)-zirconium dichloride,
diphenylsilyl(cyclopentadienyl)(9-fluorenyl)-zirconium dichloride, and
diphenylsilyl-bis(indenyl)hafnium dichloride.
33. A process as claimed in any one of the preceding claims, wherein branched polymers are formed by means of a tandem tetramerisation and polymerisation process.
34. A process as claimed in Claim 33, the tandem tetramerisation and polymerisation process being an *in situ* catalysis process wherein ethylene tetramerisation and polymerisation takes place in the same reaction medium.

35. A process as claimed in Claim 34, wherein the *in situ* catalysis process is an *in-situ* concurrent catalysis process.
36. A process as claimed in Claim 34, wherein the *in-situ* catalysis process is an *in situ* consecutive catalysis process.
37. A process as claimed in Claim 34, wherein the process includes the steps of tetramerising ethylene using a tetramerisation catalyst to produce 1-octene selectively and copolymerising *in situ* the 1-octene with ethylene using a polymerisation catalyst wherein the tetramerisation catalyst produces 1-octene in more than 30% selectivity.
38. A process as claimed in Claim 37, wherein the process includes a step of contacting the ethylene with a tetramerisation catalyst, and a step of contacting ethylene and the 1-octene derived from tetramerisation with a polymerisation catalyst, which catalyst includes a transition metal, and wherein the tetramerisation catalyst includes a transition metal and a heteroatomic ligand.
39. A process as claimed in any one of claims 5 to 38, which includes a step of combining the heteroatomic ligand with a transition metal precursor and an activator in the presence of the polymerisation catalyst.
40. A process as claimed in Claim 39, wherein the transition metal for the transition metal precursor is selected from a group consisting of chromium, molybdenum, tungsten, titanium, tantalum and nickel.
41. A process as claimed in Claim 39 or Claim 40, wherein the transition metal for the transition metal precursor is chromium.
42. A process as claimed in any one of claims 39 to 41, wherein the transition metal precursor is selected from a group comprising of an inorganic salt, organic salt, a coordination complex and organometallic complex.

43. A process as claimed in Claim 42, wherein the transition metal precursor is selected from any one of a group comprising chromium trichloride tris-tetrahydrofuran complex, (benzene)-tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl and chromium (III) 2-ethylhexanoate.
44. A process as claimed in Claim 43, wherein the transition metal precursor is selected from chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.
45. A process as claimed in any one of claims 39 to 44, wherein the transition metal from the transition metal precursor and the heteroatomic ligand are combined to provide metal/ligand ratios from about 0.01:100 to 10 000:1.
46. A process as claimed in Claim 45, wherein the transition metal precursor and the heteroatomic ligand are combined to provide metal/ligand ratios from about 0.1:1 to 10:1.
47. A process as claimed in any one of claims 39 to 46, wherein the catalyst system includes an activator selected from any one of a group consisting of organoaluminium compounds, organoboron compounds, organic salts, inorganic acids and inorganic salts.
48. A process as claimed in Claim 47 wherein the organic salts are selected from a group consisting of methyllithium bromide and methylmagnesium bromide.
49. A process as claimed in Claim 48 wherein inorganic acids and inorganic salts are selected from a group consisting of as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.
50. A process as claimed in any one of claims 39 to 49, wherein the activator is selected from alkylaluminoxanes.

51. A process as claimed in Claim 50, wherein the alkylaluminumoxane, or mixtures thereof, are selected from a group which consists of methylaluminumoxane (MAO), ethylaluminumoxane (EAO) and modified alkylaluminumoxanes (MMAO).
52. A process as claimed in Claim 51, wherein the transition metal and the aluminumoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 10 000:1.
53. A process as claimed in Claim 52, wherein the transition metal and the aluminumoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 1000:1.
54. A process as claimed in Claim 53, wherein the transition metal and the aluminumoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 300:1.
55. A process as claimed in any one of claims 50 to 54, which process includes the step of adding to the catalyst system a trialkylaluminum compound in amounts of between 0.01 to 100 mol per mol of alkylaluminumoxane.
56. A process as claimed in any one of claims 39 to 55, wherein the heteroatomic ligand and the transition metal precursor are combined at any temperature between -20°C and 250°C in the presence of an olefin.
57. A process as claimed in any one of claims 39 to 56, wherein the activator is a binuclear activator such as bisborane 1,4-(C₆F₅)₂B(C₆F₄)B-(C₆F₅)₂.
58. A process as claimed in any one of claims 4 to 57, which process includes a step of combining the polymerisation catalyst and the tetramerisation catalyst in a ratio of 0.1:1 to 1:1000 respectively.
59. A process as claimed in any one of the preceding claims 1 to 58, which process is carried out in an inert solvent.

60. A process as claimed in Claim 59 wherein ethylene is contacted with the tetramerisation catalyst system at a pressure of more than 1 barg.
61. A process as claimed in any one of the preceding 1 to 60, which process includes the step of mixing the polymerisation catalyst and the cocatalyst at any temperature between -20°C and 250°C in the presence of an olefin.
62. A process as claimed in Claim 61, wherein the temperature range is between 20°C and 100°C.
63. A process as claimed in any one of the proceeding claims where a combination of reactors is preferred where the first reactor may be a continuous stirred tank reactor and the second reactor may be a batch, continuous stirred tank reactor or a plug flow reactor.
64. A process as claimed in any one of claims 4 to 63, wherein the cocatalyst and polymerisation catalyst is combined in the ratio 0.01:100 to 10 000:1.
65. A process as claimed in any one of claims 4 to 63, wherein the cocatalyst and polymerisation catalyst is combined in the ratio of 1:1 to 100:1.
66. A process as claimed in any one of claims 1 to 65, wherein the conditions are selected such that the cocatalyst produces 1-octene in a selectivity greater than 40%.
67. A process as claimed in any one of claims 1 to 65, wherein the conditions are selected such that the cocatalyst produces 1-octene in a selectivity greater than 50%.
68. A process as claimed in any one of claims 1 to 65, wherein the conditions are selected such that the cocatalyst produces 1-octene in a selectivity greater than 60%.

69. A process as claimed in any one of claims 1 to 65, wherein the conditions are selected such that the cocatalyst produces 1-octene in a selectivity greater than 70%.
70. A process substantially as described herein.